NASA CR 65635

SACRAMENTO PLANT

INVESTIGATION OF N_2O_4 ENVIRONMENTAL EFFECTS ON SPECIALLY HEAT-TREATED Ti-6Al-4V ALLOY

Pressure Vessel Components Section
Advanced Materials Technology Department
Research and Technology Operation

Final Report

N67-29174
(ACCESSION NUMBER) (THRU) 1
25 (PAGES) (CODE)
CR-65635 (NASA CR OR TMX OR AD NUMBER) 17 (CATEGORY)
FACILITY FORM

GPO PRICE $ ______

CFSTI PRICE(S) $ ______

Hard copy (HC) 2.00

Microfiche (MF) .65

ff 653 July 65

AEROJET
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FINAL REPORT

on

INVESTIGATION OF N_2O_4 ENVIRONMENTAL EFFECTS ON SPECIALLY HEAT-TREATED Ti-6Al-4V ALLOY

to

NASA MANNED SPACECRAFT CENTER

Contract NAS 9-6015

AEROJET-GENERAL CORPORATION
RESEARCH AND TECHNOLOGY OPERATION

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FOREWORD

The research described in this report was performed for the NASA Manned Spacecraft Center, Houston, Texas, (Contract NAS 9-6015) under the technical coordination of R. Johnston and W. Castner. The research was conducted by the Research and Technology Operation of the Aerojet-General Corporation, Sacramento Plant. W. S. Tenner and J. T. Niemann of the pressure vessel components section acted as project manager and project engineer, respectively under the direction of A. V. Levy, Manager, Advanced Materials Technology Department.

ABSTRACT

The mechanical properties and N_2O_4 stress-corrosion resistance of standard and extra-low interstitial Ti-6Al-4V alloy were compared in three conditions of heat treatment. The heat treatments studied were the conventional solution-anneal-and-age and two duplex treatments which included controlled-rate cooling from above the beta transus temperature followed by the conventional treatment. The duplex treatments produced an acicular rather than an equiaxed alpha phase. Tensile properties were measured using unnotched sheet specimens. Similar specimens were used to evaluate stress-corrosion resistance at applied stress levels between 85 an 130 ksi. The specimens were subjected to N_2O_4 under a pressure of 250 psig and at temperatures of 105 and 160°F until failure occurred or a maximum of 30 days. Fracture toughness was evaluated qualitatively using precracked Charpy impact specimens.

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I. INTRODUCTION

Early in 1965, the Aerojet-General Corporation conducted an independent investigation to determine the effects of microstructural variation on the mechanical properties of Ti-6Al-4V alloy. It was found that conventionally heat-treated material had a precracked Charpy impact value of 526 in.-lb/in.^{2} and that this could be increased to 813 in.-lb/in.^{2} without effectively changing the tensile strength by changing the alpha phase in the microstructure from an equiaxed to an acicular form. This change was accomplished by slow cooling from above the beta transus temperature and then solution annealing and aging in the conventional manner.

To further investigate the possible advantages of the acicular or platelet-alpha microstructure, a limited stress-corrosion study was conducted in a three percent sodium chloride solution using fatigue precracked center-notch tensile specimens. A significant improvement in stress corrosion resistance was observed. Samples heat-treated by both the conventional treatment and duplex treatments (acicular alpha) were machined with a 2-1/2-in. wide test section and an initial crack width of 0.75 in. Conventionally heat-treated samples with an equiaxed alpha microstructure failed after four minutes when stressed to 30 ksi. Under similar test conditions, specimens heat-treated to produce a platelet-alpha microstructure withstood 4000 min exposure without failure. In view of this superior performance, the research described in this report was undertaken to determine if a comparable improvement in resistance to N_2O_4 exposure could be gained by altering the form of the alpha phase in the Ti-6Al-4V alloy through heat treatment.

II. SUMMARY

Tensile, fracture-toughness, and stress-corrosion studies were conducted on both standard and extra-low interstitial content Ti-6Al-4V alloy. In both of these materials, the conventional solution anneal-and-age heat-treatment and two duplex heat-treatments were evaluated. The duplex procedures consisted of controlled slow-cooling from above the beta-transus temperature followed by the conventional treatment. The fracture toughness tests showed that the duplex heat treatment improved the toughness of the ELI material but not that with standard interstitial content. Also, it was found that resistance to stress-corrosion cracking in N_2O_4 was not improved by the duplex treatments in either ELI or standard interstitial content Ti-6Al-4V alloy.

III. TECHNICAL DISCUSSION

The primary objective of this program was to determine whether or not the fracture toughness and N_2O_4 stress-corrosion resistance of Ti-6Al-4V could be improved through the application of special heat treatments to control the form of the alpha phase. Microstructures with the alpha phase in platelet rather than equiaxed form were produced by two duplex heat treatments. Specimens machined from material heat-treated by these duplex procedures and by the conventional procedure were compared on the basis of mechanical properties and resistance to stress-corrosion in N_2O_4.

A. SELECTION OF HEAT TREATMENTS

The first heat treatment studies were conducted on 1-in. x 1-in. x 1/2-in. samples cut from a one-inch thick dome-shaped forging of standard interstitial content Ti-6Al-4V alloy. Throughout the program the heat treatments were carried out in a helium atmosphere to minimize contamination. Several preliminary tests were conducted using various heat treatments in an effort to produce microstructures characterized by acicular alpha. The desired microstructure was attained under some conditions but the results were not consistent. Additional tests indicated that the inconsistency was due to variations in the amount of working within the forging. Because of this, the directionality effects from forging were not eliminated in some samples after holding for 18 hr at 1790°F. Consequently, no further efforts were made to develop the desired microstructure in the forged alloy.

The next heat-treating studies were conducted on samples cut from 1-in. thick ELI plate with the following interstitial content: 0.023%C, 0.009%N, 0.0065%H and 0.07%O. Two samples, 1-in. x 1-in. x 4-in. then were heated to 1840°F, held for 1 hr, cooled at 45°F and 50°F/hr to 1200°F, air cooled to room temperature and then solution annealed by quenching from 1750°F after holding for 30 minutes. Metallographic examination showed that both slow cooling rates of 45 and 50°F/hr had produced a platelet-alpha microstructure of the desired configuration. Two additional tests were made at cooling rates of 40 and 55°F/hr to determine if the cooling rate significantly changed the appearance of the platelet alpha. These samples were given a duplex treatment and aged at 1000°F for eight hours. Their microstructure was similar to the samples cooled at intermediate rates.

The final heat treatment studies were made on sections cut from a 52-in.-dia Minuteman rocket motor case. This case is produced by ring-roll forging and machined to a final thickness of 0.104 in. The specified interstitial content of the material used for Minuteman cases is: 0.10% max C, 0.05% max N, 0.0125% max H and, 0.12 to 0.20% O.

Sections of the Minuteman case were given the same treatments used on the ELI plate material with cooling rates of 40 and 55°F/hr in the first step of the duplex cycle. Metallographic examination showed that this standard interstitial material also had a platelet alpha microstructure but the platelets were somewhat coarser than with ELI material. Microstructure of both the standard and extra-low interstitial materials are compared in Figure 1 for the conventional and two duplex heat treatments.

B. EVALUATION OF MECHANICAL PROPERTIES

The heat-treating studies indicated that cooling at rates between 40 and 55°F/hr through the transformation range produced similar platelet alpha structures. The two extreme cooling rates investigated were selected for further evaluation to determine if these cooling rates affected mechanical properties even though they did not produce gross microstructural differences.

Tensile and fracture toughness properties were investigated for both the Minuteman standard interstitial material and the ELI 1-inch thick plate. The specimen designs and orientation are shown in Figures 2 and 3. The results of the mechanical property tests are given in Table 1. These test results indicate that the method of heat treatment did not affect the strength properties of the ELI plate. All three treatments produced a nominal yield strength of 130 ksi and a tensile strength of about 150 ksi. However, the treatments did influence ductility; the conventionally treated specimen had higher elongation values than the duplex treated material, (10 vs 6%).

The strength properties of the standard interstitial material were significantly higher than those measured in ELI samples. Specimens from the Minuteman chamber heat-treated in the conventional manner and by the duplex cycle with a cooling rate of 55°F/hr exhibited a yield strength of about 170 ksi and a tensile strength of 185 ksi; the 40°F/hr cooling rate duplex cycle resulted in 10 ksi lower strength. The elongation values of specimen from all three treatments were about six percent.

From the standpoint of toughness, the ELI material exhibited significantly higher W/A values than did standard interstitial material. Also, the duplex treatments improved the toughness of the ELI material from 1427 in.-lb/in.^{2} to about 2000 in.-lb/in.^{2}. On the other hand, the toughness of the standard interstitial material was not improved by the duplex heat treatment. Interstitial oxygen content may determine whether or not the toughness of Ti-6Al-4V alloy can be improved by the presence of acicular rather than equiaxed alpha. This possibility is indicated by comparing the toughness values of heats with different oxygen contents given a duplex treatment (40°F/hr cooling rate) and the conventional treatment. This comparison is given below for the two heats of material studied in this investigation and the heat used in the initial Aerojet-General program.

		Precracked Charpy Value, in.-lb/in.^{2}		
Material	Oxygen (ppm)	Conventional Treatment	Duplex Treatment	Increase
Current Program ELI	700	1427	2014	587
Initial Program Standard	1100	526	813	237
Current Program Standard	1200 to 2000 (Specification limits)	481	342	-139

Apparently, as the oxygen increases, the alpha platelets become increasingly embrittled and are no longer capable of blunting a crack front.

Electron fractographs taken from selected Charpy specimen fracture surfaces are shown in Figure 4. The fractograph which represents the toughest condition, a duplex treatment with a 40°F/hr cooling rate, consists of large tear dimples. For the same extra-low interstitial material heat-treated in the conventional manner, the tear dimples seem somewhat smaller but the general morphology is the same. In the lowest toughness condition, which was standard interstitial material given a duplex treatment with a 55°F/hr cooling rate, the dimple size was still about the same but these areas were fewer in number and there was a tendency for them to consist of more nearly equiaxed dimples. The fact that the shape of the dimples changes from an elongated tear type in the ELI material to a relatively equiaxed normal type in the standard interstitial content material indicates that the ratio of the maximum principal strains is decreasing. In a Charpy test, tear-type dimples would be expected in a tough material and equiaxed dimples in a less tough structure which indicates that the alpha platelets may become embrittled as the oxygen content is increased.

C. STRESS-CORROSION STUDIES

The final part of the investigation was directed toward determining whether or not resistance of the Ti-6Al-4V alloy to stress-corrosion cracking in N_2O_4 could be improved by using the duplex rather than the conventional heat treatment. For this purpose, specimens were stressed to various levels and exposed to N_2O_4. As before, both standard and extra-low interstitial material and the conventional and two duplex heat treatments were compared.

In the stress-corrosion tests smooth tensile specimens as shown in Figure 2 were evaluated. Fatigue precracked specimens were considered more desirable so that fracture mechanics concepts could be applied to the resultant data but because all previous studies of Ti alloy - N_2O_4 compatibility used smooth specimens, this same approach was followed so that the test results could be more readily compared to those of previous investigations. Each specimen was instrumented with a strain gage, placed in a tensile machine, loaded to the predetermined stress level and the corresponding strain reading recorded. The load was then released and the specimen placed in a gang fixture as shown in Figure 5 and torqued to the previously recorded strain value. Each fixture held five specimens and all the samples in the same fixture were stressed to the same level. Three of the five samples represented the duplex treatment and the other two the conventional heat treatment.

Each fixture was then placed into a sealed container. The individual containers were placed in a controlled temperature water bath as shown in Figure 6 and manifolded for filling with N_2O_4 and pressurizing to 250 psig. During the exposure period, each container was opened daily for the first seven days and then twice weekly until all the specimens had failed or until 30 days had elapsed. After each inspection the containers were refilled with fresh N_2O_4. During the course of the investigation, several chemical analyses of the N_2O_4 were made. The NO content never exceeded 0.01% and the highest water content measured was 0.03%.

The first stress-corrosion tests were made on specimens from extra-low interstitial material at a test temperature of 105°F and stress levels of 95 and 85 ksi. Higher stress levels were not used because of the low yield strength of this material (130 ksi). Under these test conditions, none of the samples failed in the 30-day test. Then the test temperature was increased to 160°F and the exposure continued on the same samples. At the higher temperature, failures were observed after 50 hr exposure, and all but one sample had failed after a test period of 500 hr, or less.

Standard interstitial material was tested in a similar manner at stress levels of 130, 115 and 95 ksi with no failures observed after 14 days at 105°F; but failure occurred in less than 50 hours when the temperature was increased to 160°F.

The results of the stress-corrosion tests are summarized in Table 2 and shown in Figure 7. These data show that the resistance of Ti-6Al-4V to stress-corrosion cracking in N_2O_4 was neither improved by the duplex treatment, nor was there a great difference in the performance of the standard and ELI material at the same stress level. A typical specimen failure is shown in Figure 8.

In general, the stress-corrosion data agrees with the results of other investigations in which failures were reported in 90 hr or less for specimens subjected to N_2O_4 at 160°F at stress levels between 90 and 140 ksi.[1] However, the findings were contrary to expectations that were based on the previous results of salt water exposure tests at Aerojet-General in which conventionally heat-treated samples failed after four minutes exposure and duplex treated samples withstood 4000 minutes without failure. In the earlier study, fatigue precracked specimens were used and provided a measure of the time required for an existing defect to grow to critical size and result in catastrophic failure. As a result, the difference in crack growth rates was studied in the NaCl tests and found to vary significantly with microstructures.

On the other hand, smooth specimens of the type used in this program measure the time required to initiate a crack as well as propagate it. It is possible that the time for flaw initiation was long and the time for propagation short. As a result, any improvement in resistance to rate of slow crack growth resulting from microstructural difference might go unnoticed because of the relatively long time between inspection periods which could greatly exceed the interval needed for crack propagation. Another possibility is that resistance to crack growth was improved by changing the microstructure but the presence of the alpha platelets presented more sites for flaws to

(1) Jackson, J. D. and Boyd, W. K., "Corrosion of Titanium", DMIC Memorandum 218, Defense Metals Information Center, Battelle Memorial Institute, Columbus, Ohio (Sept. 1, 1966).

initiate and counteracted the improved property by shortening the incubation time. In either case, if any improvement from the acicular alpha did exist, it was not sufficient to be of practical significance.

Another likely cause for a difference in behavior in NaCl and N_2O_4 is the basic difference in environments. According to DMIC Memorandum 218, thermodynamic considerations of possible chemical reactions between Ti-6Al-4V alloy and N_2O_4 and its impurities minimize electrochemical action as a failure mechanism. This would not be the case in a 3% NaCl solution. Thus, the mechanisms of crack initiation and propagation may be different in both systems so that a method of eliminating stress-corrosion cracking in one environment could be ineffective in the other.

IV. CONCLUSIONS

The results of this investigation indicate the following:

(1) Heat treatments which produce acicular rather than equiaxed alpha phase in Ti-6Al-4V alloy can improve fracture toughness.

(2) Improvement in toughness may be a function of the interstitial oxygen content; the greatest improvements have been observed on extra-low interstitial material with no improvement noted in higher oxygen content material.

(3) The improved toughness in the lower oxygen heats was not accompanied by a decrease in strength.

(4) Resistance to stress corrosion cracking in N_2O_4 is not improved by duplex heat treatments.

TABLE 1

MECHANICAL PROPERTIES OF TI-6AL-4V ALLOY HEAT-TREATED BY CONVENTIONAL AND DUPLEX TREATMENTS

Heat-Treatment	Material Type	Specimen	0.2% Offset Yield Strength, ksi	Tensile Strength, ksi	Elongation in 1-in.,%	Toughness, Pre-Cracked Charpy Impact, W/A, in-lbs/in.^{2}
Conventional (1750°F/30 min, water quench. Age 1000°F/8 hr)	Standard Interstitial	1	165.7	187.7	5.4	460
		2	169.7	187.7	5.4	460
		3	172.0	190.7	5.4	522
		Aver.	169.1	188.7	5.4	481
	Extra-Low Interstitial	1	128.8	147.4	8.5	1245
		2	133.2	150.0	12.0	1518
		3	131.5	151.3	10.5	1519
		Aver.	131.2	149.2	10.3	1427
Duplex A (1840°F/1 hr, cool 40°F/hr to 1200°F, air cool to room temp Re-heat 1750°F/30 min, water quench. Age 1000°F/8 hr)	Standard Interstitial	1	162.8	175.4	3.0	316
		2	159.6	178.5	3.1	344
		3	160.3	177.5	3.1	368
		Aver.	160.9	177.8	3.1	342
	Extra-Low Interstitial	1	130.9	150.0	8.5	2128
		2	132.5	150.4	5.0	2004
		3	134.1	150.9	5.0	1911
		Aver.	132.5	150.4	6.2	2014
Duplex B (1840°F/1 hr, cool 55°F/hr to 1200°F, air cool to room-temp Re-heat 1750°F/30 min, water quench. Age 1000°F/8 hr)	Standard Interstitial	1	166.7	184.6	5.2	329
		2	169.7	185.4	5.2	556
		3	-	-	-	381
		Aver.	168.2	185.0	5.2	422
	Extra-Low Interstitial	1	131.0	150.8	7.0	1826
		2	131.2	149.6	6.0	2060
		3	129.0	148.4	6.5	1983
		Aver.	130.4	149.0	6.5	1956

Table 1

TABLE 2

RESULTS OF STRESS-CORROSION TESTS CONDUCTED ON TI-6AL-4V ALLOY HEAT-TREATED BY CONVENTIONAL AND DUPLEX TREATMENTS IN N_2O_4 AT 250 PSIG AND 160°F

Heat-Treatment	Applied Stress, ksi	Standard Interstitial Specimen	Standard Interstitial Lifetime, hr	Extra-Low Interstitial Specimen	Extra-Low Interstitial Lifetime, hr
Conventional (1750°F/30 min, water quench. Age 1000°F/8 hr)	130	1	65-87	-	
		2	65-87	-	
		3	87-158	-	
		4	87-158	-	
	115	1	94-166	-	
		2	94-166	-	
		3	94-166	-	
		4	166-262	-	
	95	1	94-166	1	71-148
		2	94-166	2	71-148
		3	166-262	3	71-148
		4	166-262	4	336-407
	85	-		1	71-148
		-		2	407-503
		-		3	407-503
		-		4	407-503
Duplex A (1840°F/1 hr, cool 40°F/hr to 1200°F, air cool to room temp	130	1	23-46	-	
		2	46-65	-	
		3	46-65	-	
Re-heat 1750°F/30 min, water quench. Age 1000°F/8 hr)	115	1	28-52	-	
		2	52-71	-	
		3	72-94	-	
	95	1	52-71	1	26-50
		2	94-166	2	71-148
		3	94-166	3	71-148
	85	-		1	71-148
		-		2	336-407
		-		3	336-407
Duplex B (1840°F/1 hr, cool 55°F/hr to 1200°F, air cool to room-temp	130	1	65-87	-	
		2	87-158	-	
		3	87-158	-	
Re-heat 1750°F/30 min, water quench. Age 1000°F/8 hr)	115	1	28-52	-	
		2	28-52	-	
		3	94-166	-	
	95	1	94-166	1	26-50
		2	94-166	2	71-148
		3	94-166	3	71-148
	85	-		1	503
		-		2	336-407
		-		3	336-407

Notes:

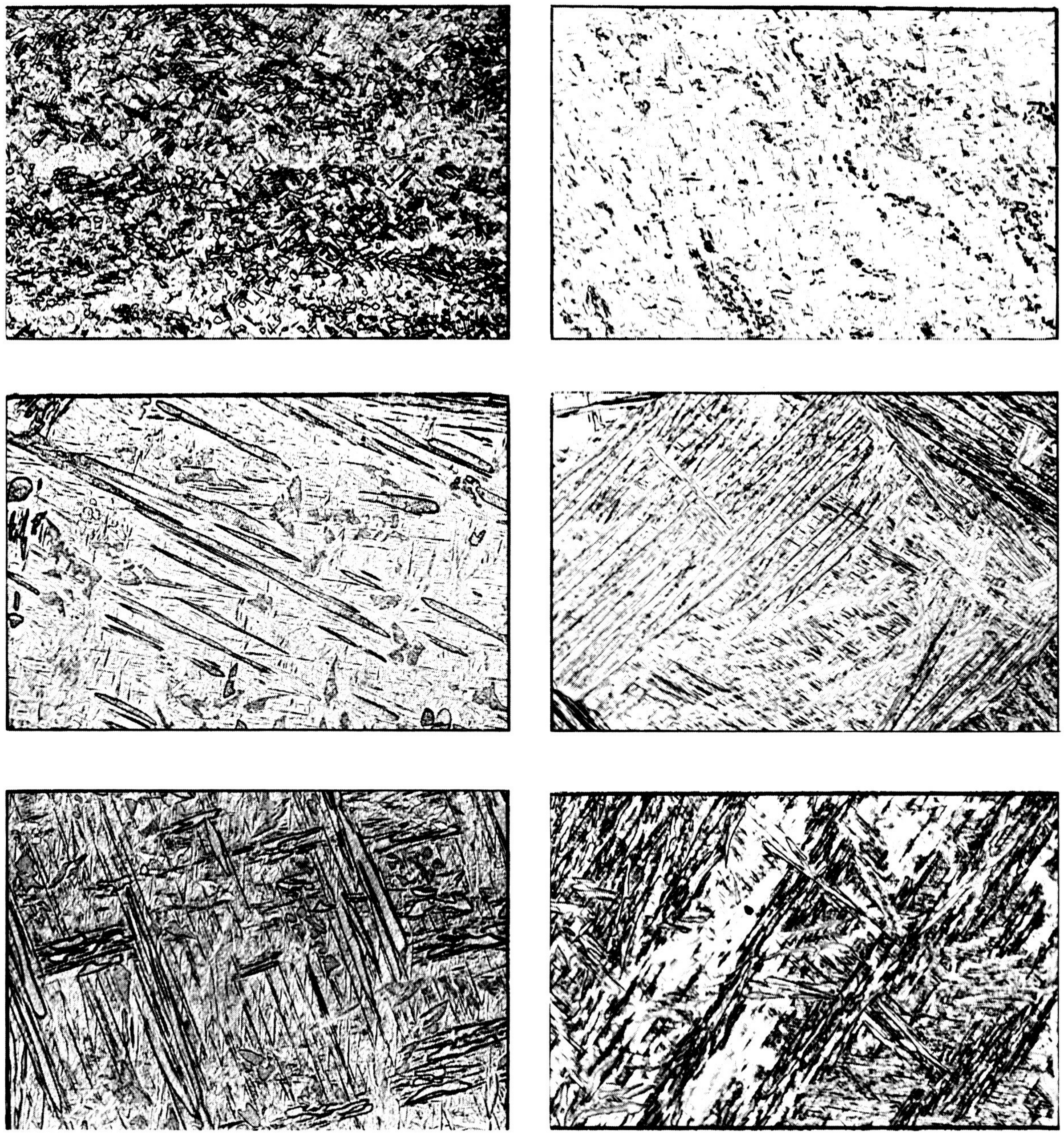
1. Standard interstitial specimens were exposed 14 days
   Extra-Low Interstitial specimens were exposed 30 days at 105°F, 250 psig, and indicated stress level without failure to exposure at 160°F
2. Lifetime hours are elapsed time of 160°F exposure to start and completion of test interval during which failure occurred

Standard Interstitial | Extra-Low Interstitial

Conventional Heat Treatment

Duplex Treatment (40°F/hr Cool to 1200°F)

Duplex Treatment (55°F/hr Cool to 1200°F)



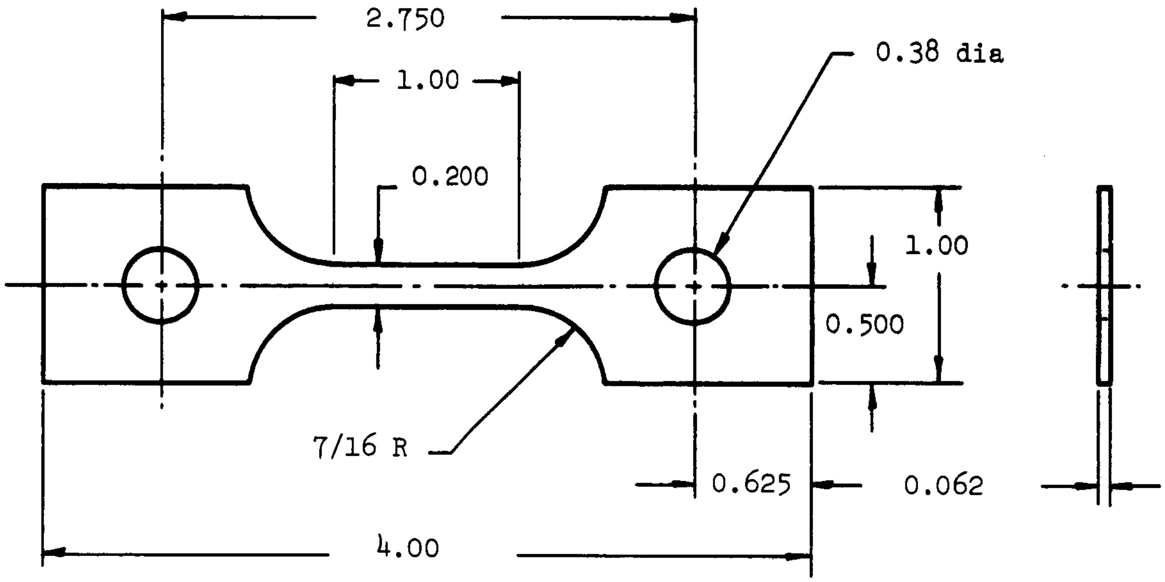
Etchant: 2% HF, 5% HNO_3, 93% H_2O

Conventional Treatment: 1750°F/30 min., water quench, age 1000°F/8 hr

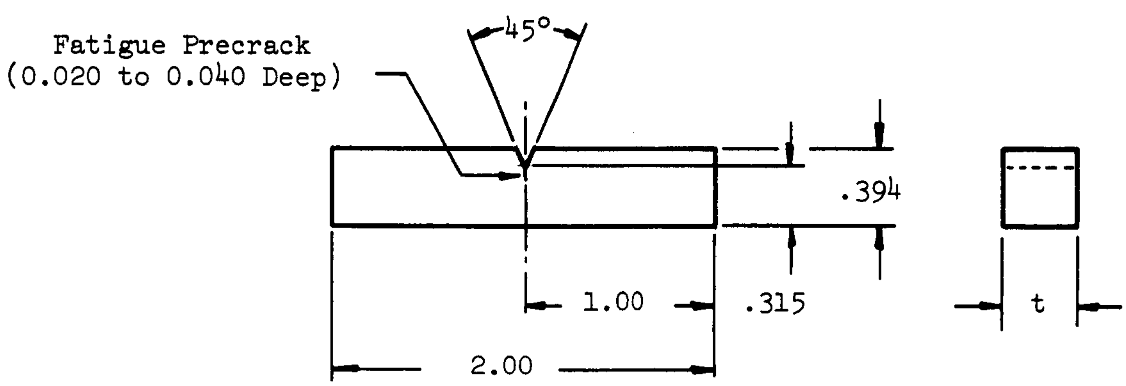
Duplex Treatment: 1840°F/1 hr, controlled-rate cool to 1200°F, air cool room temp Reheat 1750°F/30 min, water quench, age 1000°F/8 hr

Effect of Heat Treatment on Microstructure of Ti-6Al-4V Alloy

Figure 1



Tensile and Stress-Corrosion Specimen



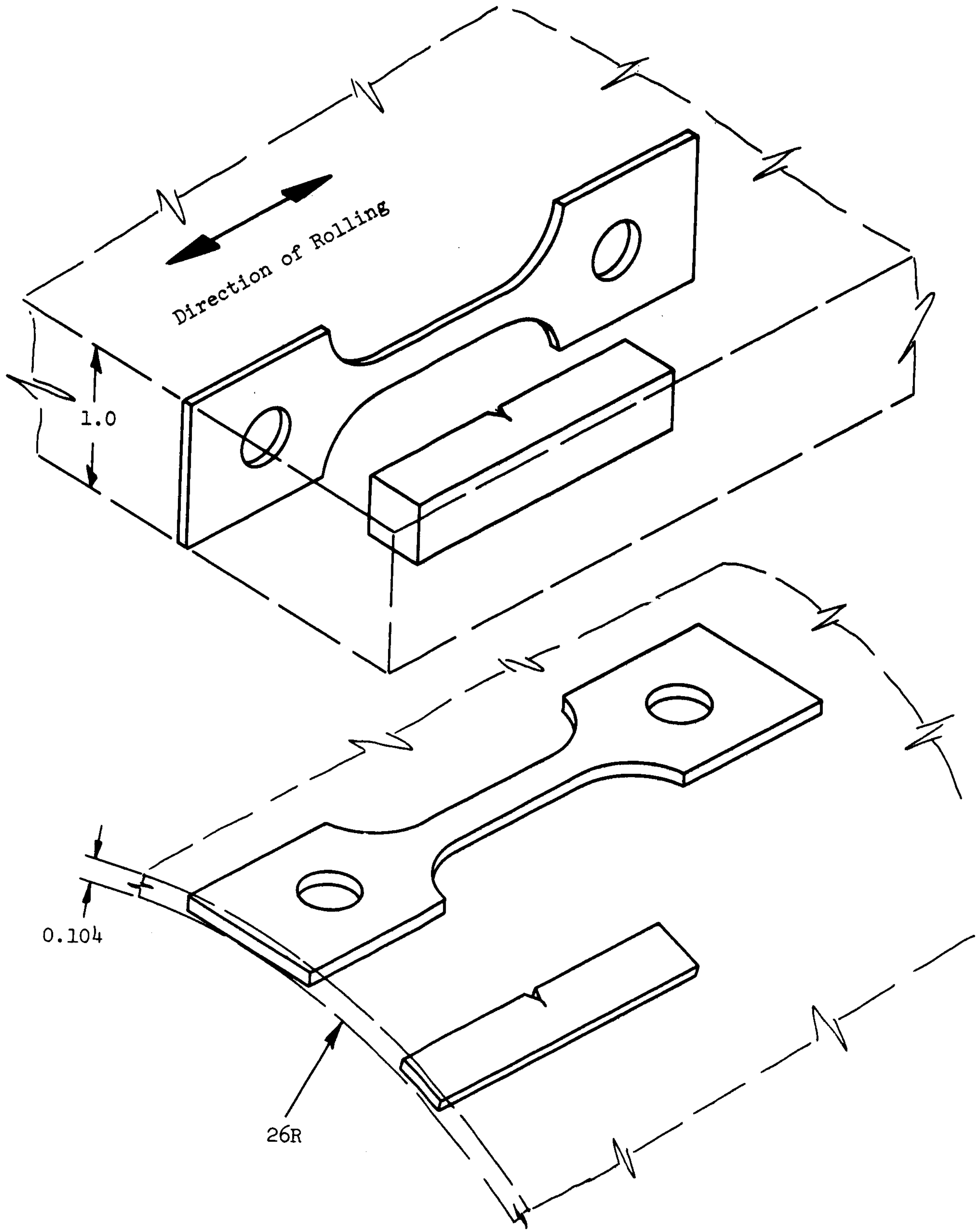
t = 0.394 for specimens from 1-in. thick ELI plate

t = 0.080 for specimens from Minuteman Case

Precracked Charpy Impact Specimen

Design of Specimens Used to Compare Mechanical Properties and Stress-Corrosion Resistance of Ti-6Al-4V Alloy Heat-Treated by Conventional and Duplex Treatments

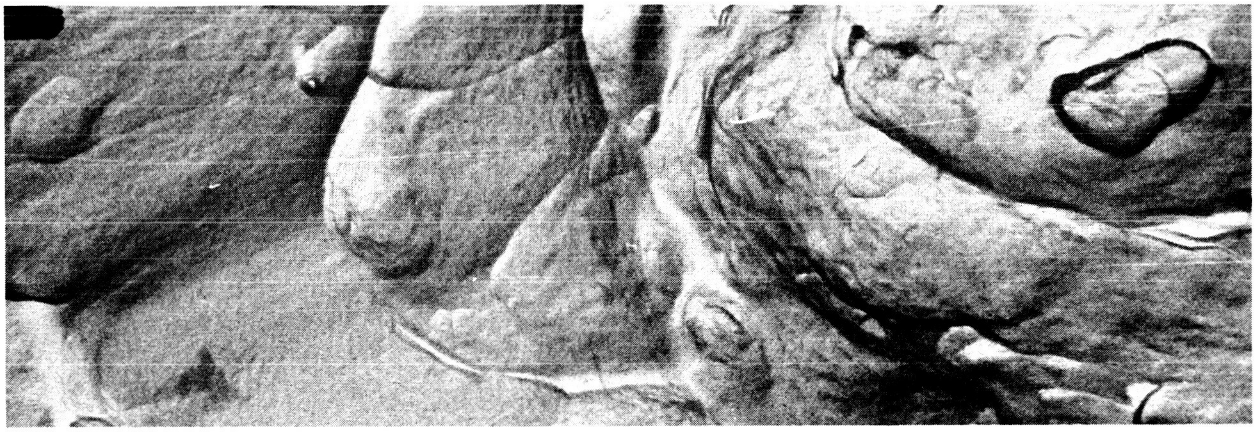
Figure 2



Orientation of Test Specimens in Ti-6Al-4V ELI Plate and in Standard Interstitial Minuteman Case

Figure 3

$\frac{W}{A} = 2014$ in-lbs/in.^{2}



10,000X

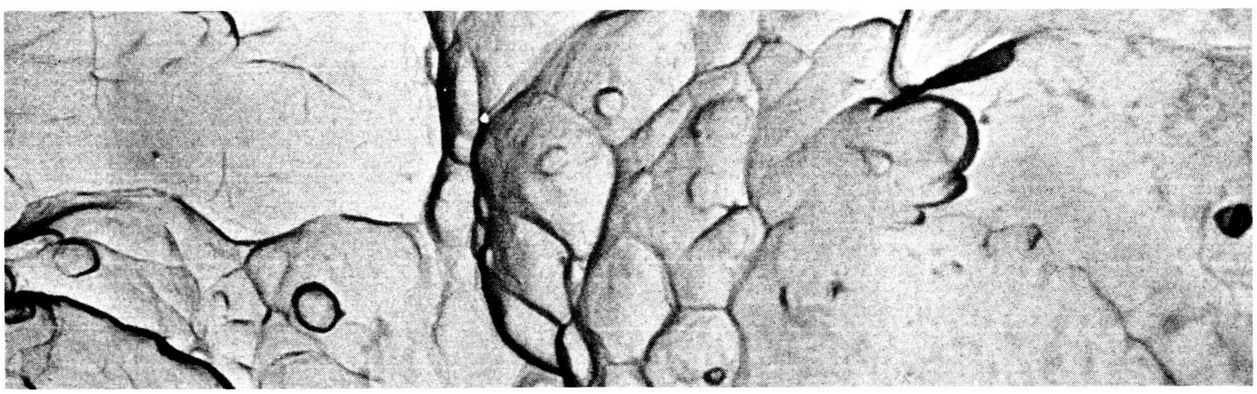
Extra-Low Interstitial
Duplex Treatment (40°F/hr Cool)

$\frac{W}{A} = 1427$ in-lbs/in.^{2}

7,200X

Extra-Low Interstitial
Conventional Treatment

$\frac{W}{A} = 422$ in-lbs/in.^{2}

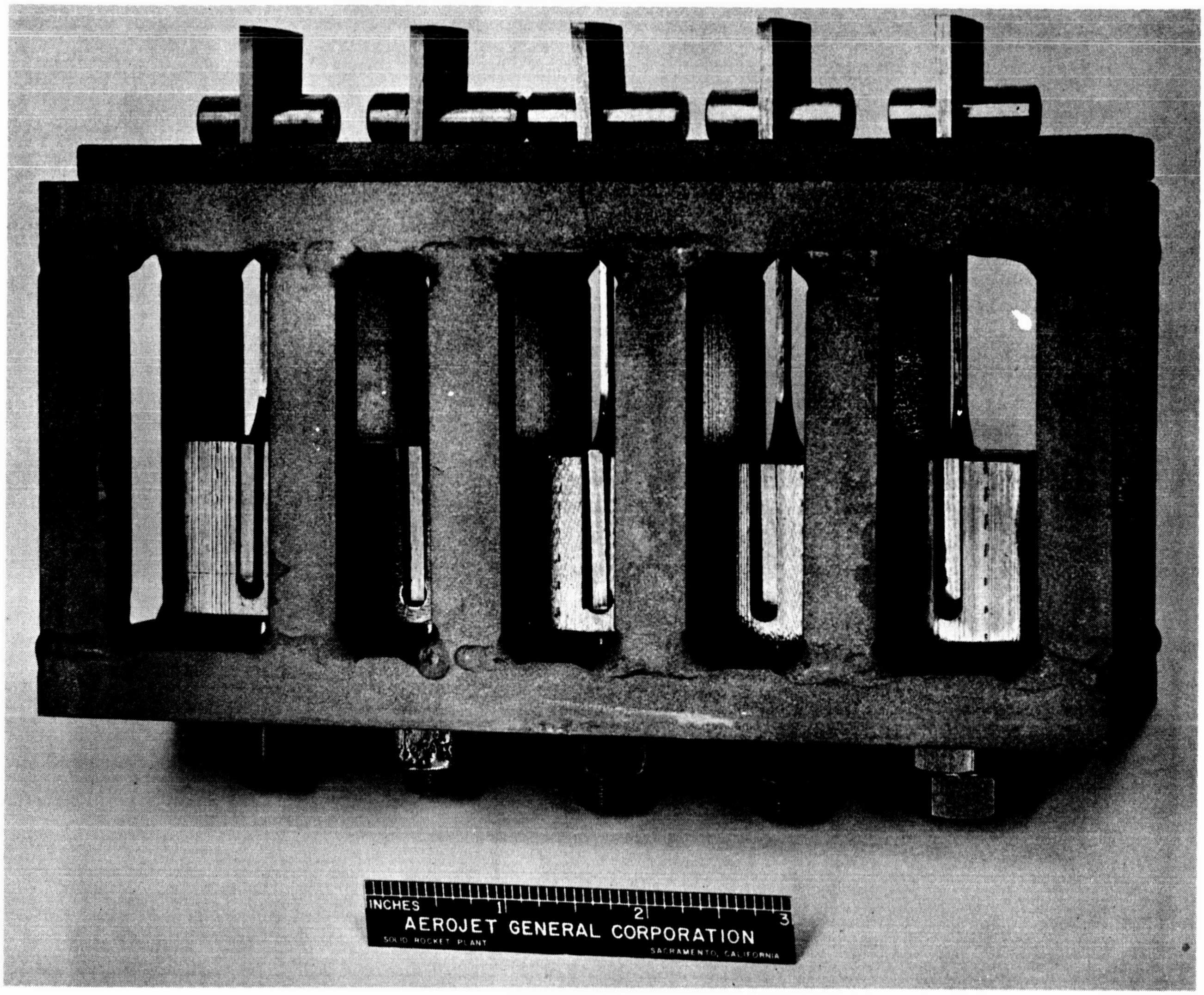


10,000X

Standard Interstitial
Duplex Treatment (55°F/hr Cool)

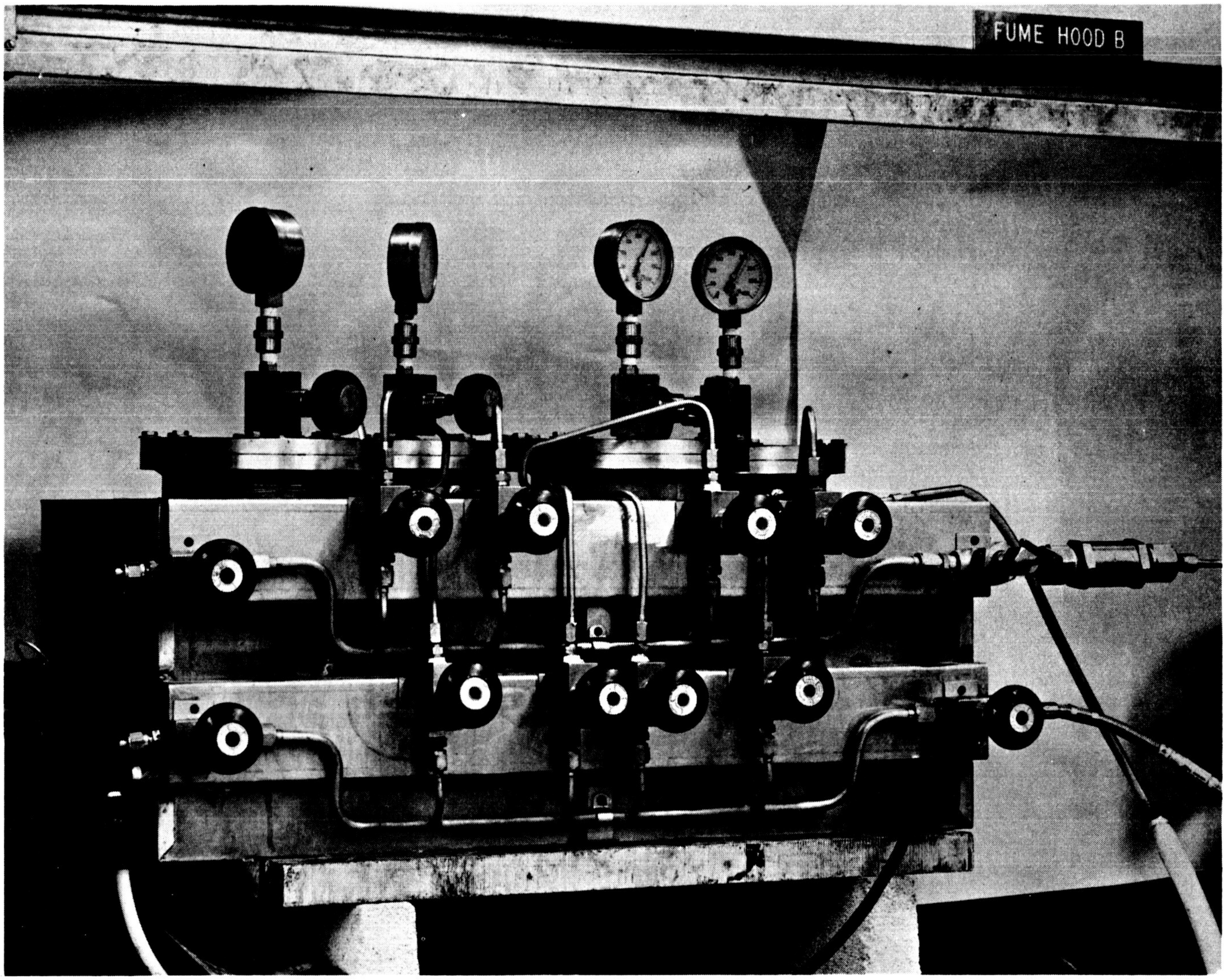
Electron-Microscope Fractographs of Ti-6Al-4V Alloy Heat-Treated by Conventional and Duplex Treatments

Figure 4



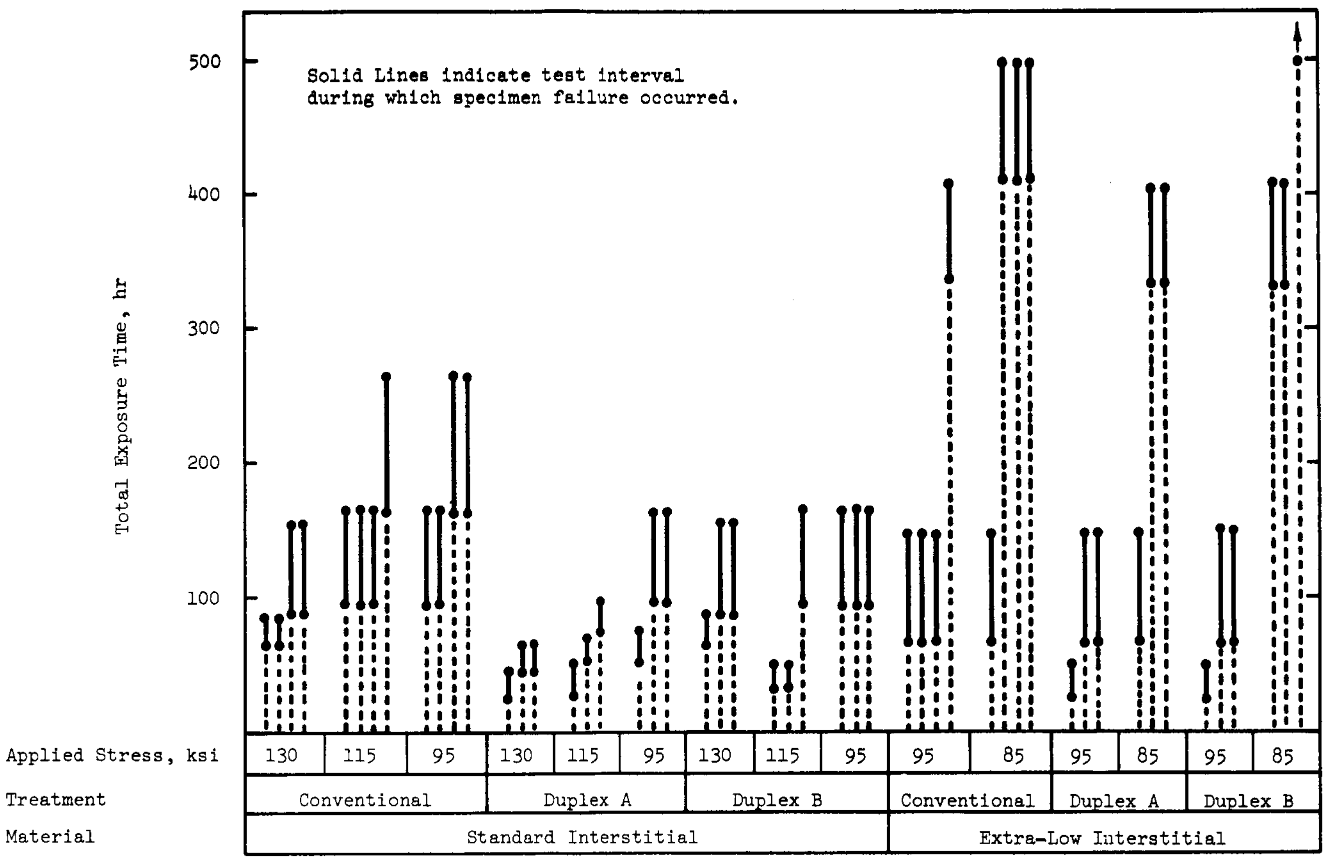
Stress-Corrosion Test Loading Fixture

Figure 5



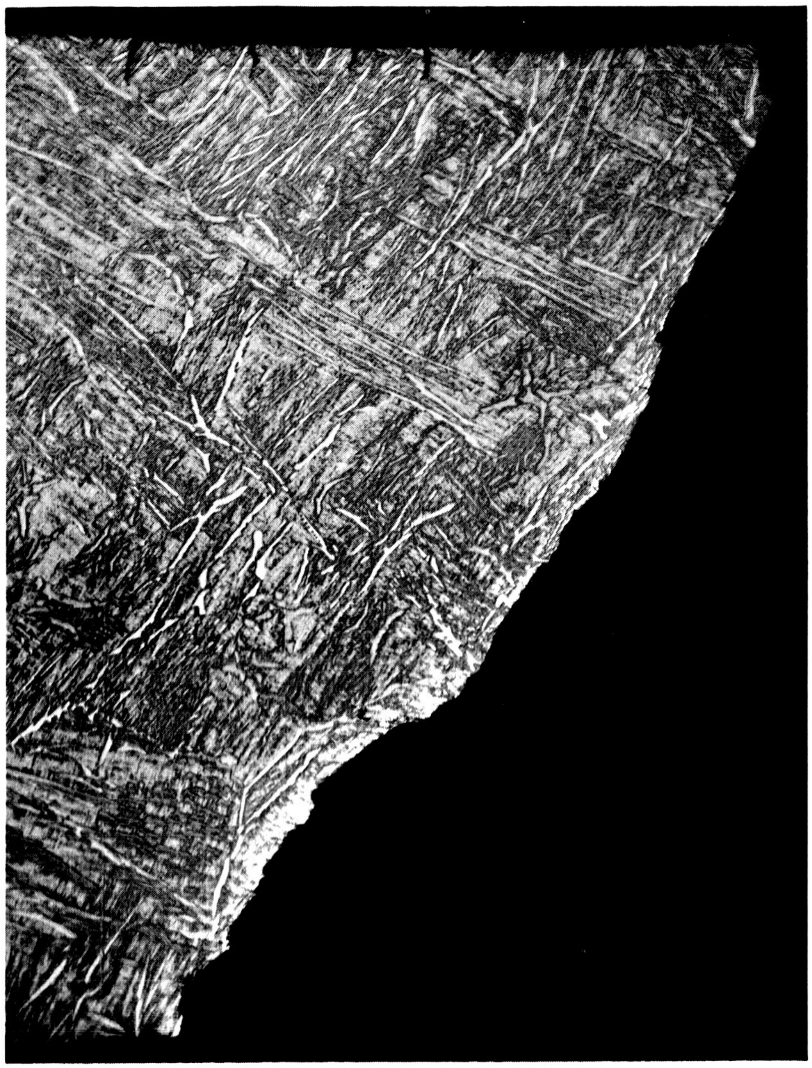
Stress-Corrosion Test Apparatus

Figure 6



Comparison of Stress-Corrosion Susceptibility in N_2O_4 at 160°F of Standard and Extra-Low Interstitial Content Ti-6Al-4V Alloy Subjected to Conventional and Duplex Heat Treatments

Figure 7



100X

Typical Stress-Corrosion Failure in Ti-6Al-4V ELI Alloy Heat-Treated by Duplex Treatment (55°F/hr Cooling Rate) in N_2O_4 at 160°F

Figure 8